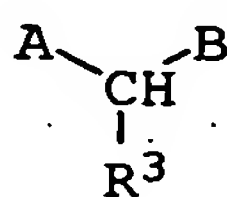


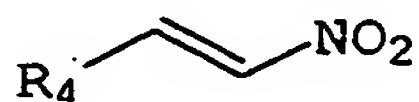
## WHAT IS CLAIMED IS:

1. A method of preparing a compound having a quaternary carbon atom of desired stereoselectivity comprising reacting a compound having a structural formula (I)



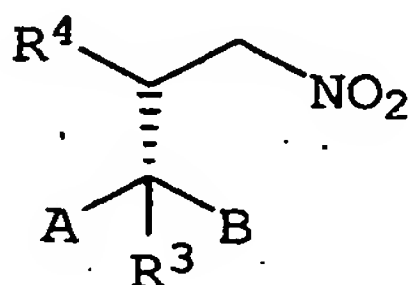
(I)

with a nitroolefin of structural formula (II)



(II)

to form a nitro compound of structural formula (III) or its enantiomer



(III)

wherein A is selected from the group consisting of C(=O)OR<sup>1</sup>, C(=O)N(R<sup>5</sup>)<sub>2</sub>, C(=O)SR<sup>5</sup>, CN, NO<sub>2</sub>, and SO<sub>2</sub>R<sup>5</sup>; B is selected from the group consisting of C(=O)OR<sup>2</sup>, C(=O)N(R<sup>5</sup>)<sub>2</sub>, C(=O)SR<sup>5</sup>, and CN; R<sup>1</sup> is selected from the group consisting of C<sub>1-4</sub>alkyl, hydro, and M; R<sup>2</sup> is selected from the group consist-

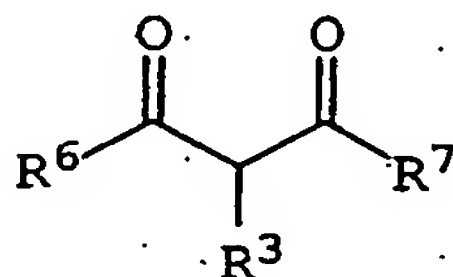
- 51 -

ing of hydro, M, alkoxyalkyl, alkyl, cycloalkyl, aryl, C<sub>1-3</sub>alkylenearyl, heteroaryl, and C<sub>1-3</sub>alkyleneheteroaryl; R<sup>3</sup> is selected from the group consisting of C<sub>1-4</sub>alkyl, alkoxy, acylamino, halo, alkylthio, allyl, C<sub>1-3</sub>alkylenearyl, and cyanoC<sub>1-3</sub>alkyl; R<sub>4</sub> is selected from the group consisting of unsubstituted or substituted aryl and heteroaryl; R<sup>5</sup>, independently, is selected from the group consisting of hydro, C<sub>1-4</sub>alkyl, cycloalkyl, aryl, C<sub>1-3</sub>alkylenearyl, heteroaryl, and C<sub>1-3</sub>alkyleneheteroaryl; and M is an alkali metal cation or an alkaline earth metal cation; and

said reaction performed in the presence of a base and a catalyst complex comprising a ligand and a metal complex.

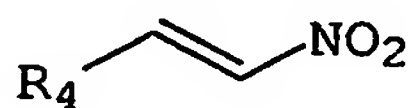
- 52 -

2. A method of preparing a compound having a quaternary carbon atom of desired stereoselectivity comprising reacting an  $\alpha$ -substituted  $\beta$ -dicarbonyl compound of structural formula (Ia)



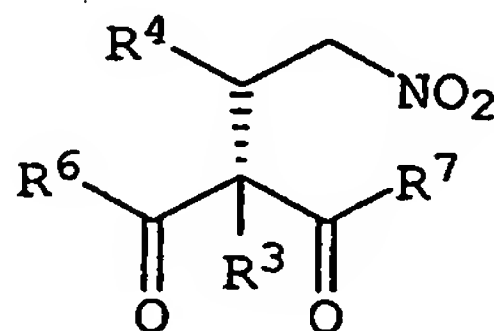
(Ia)

with a nitroolefin of structural formula (II)



(II)

to form a nitro compound of structural formula (IIIa) or its enantiomer



(IIIa)

wherein  $\text{R}^6$  is alkoxy;  $\text{R}^7$  is selected from the group consisting of alkoxy, alkoxyalkyl, alkyl, cycloalkyl, aryl,  $\text{C}_{1-3}$ alkylenearyl, heteroaryl,  $\text{C}_{1-3}$ alkyleneheteroaryl;  $\text{R}^3$  is selected from the group consisting of  $\text{C}_{1-4}$ alkyl, alkoxy, acylamino, halo, alkylthio, allyl,  $\text{C}_{1-3}$ alkylenearyl, and cyano- $\text{C}_{1-3}$ alkyl; and  $\text{R}^4$  is selected from the group consist-

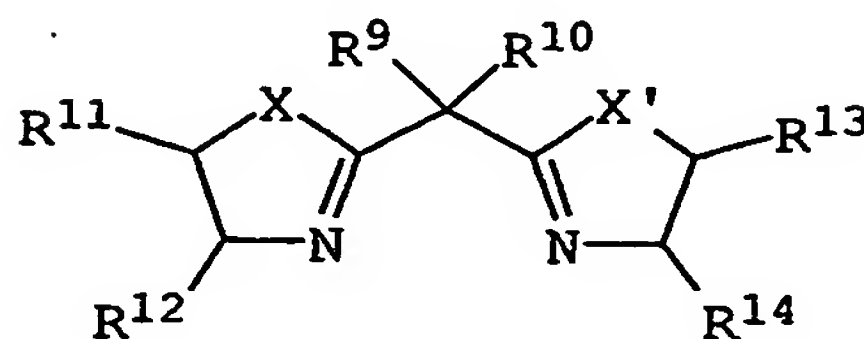
- 53 -

ing of unsubstituted or substituted aryl and hetero-aryl;

said reaction performed in the presence of a base and a catalyst complex comprising a ligand and a metal complex.

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3. The method of claim 1 or 2 wherein the ligand has a structural formula (VI)



(VI)

wherein  $R^9$  and  $R^{10}$ , independently, are selected from the group consisting of hydro, alkyl, aryl, and  $C_{1-3}$ alkylenearyl, or  $R^9$  and  $R^{10}$  are taken together to form a 3-, 4-, 5-, or 6-membered cycloalkyl ring or a bicyclic ring;

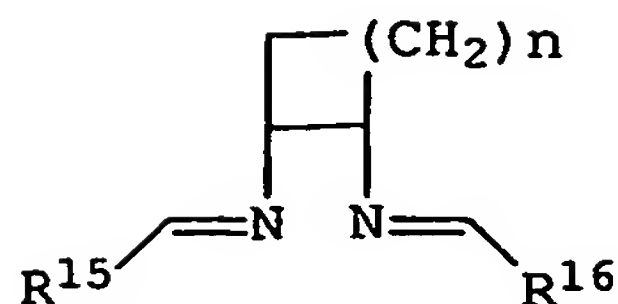
X and X', independently, are selected from the group consisting of oxygen, sulfur, and nitrogen;

$R^{11}$  and  $R^{12}$ , independently, are selected from the group consisting of hydro, alkyl,  $C_{1-3}$ alkylenearyl, and aryl, or  $R^{11}$  and  $R^{12}$  are taken together with the ring to which they are attached to form a bicyclic or tricyclic fused ring; and

$R^{13}$  or  $R^{14}$ , independently, are selected from the group consisting of hydro, alkyl,  $C_{1-3}$ alkylenearyl, and aryl, or  $R^{13}$  and  $R^{14}$  are taken together with the ring to which they are attached to form a bicyclic or tricyclic fused ring;

or has a structural formula (VII),

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(VII)

wherein  $n$  is 1-3, and  $\text{R}^{15}$  and  $\text{R}^{16}$ , independently, are selected from the group consisting of alkyl, aryl, and  $\text{C}_{1-3}$ alkylenearyl.

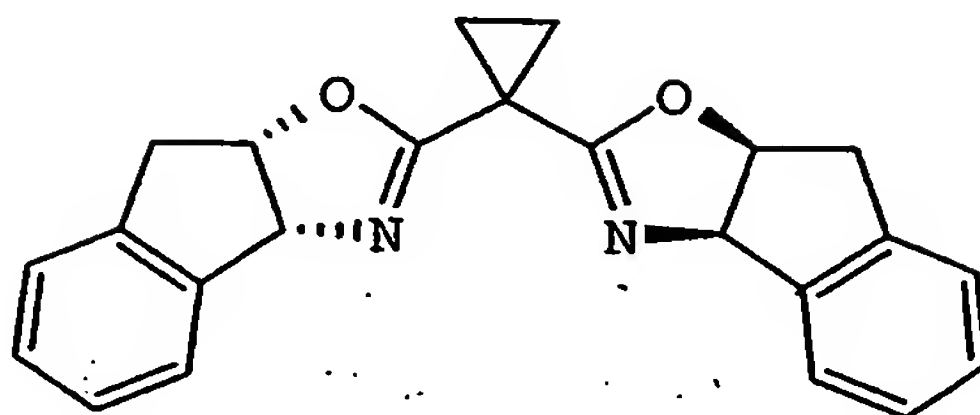
4. A method of claim 1 or 2 wherein the metal complex is selected from the group consisting of magnesium perchlorate, magnesium trifluoromethanesulfonate, copper trifluoromethanesulfonate, zinc trifluoromethanesulfonate, lanthanum trifluoromethanesulfonate, nickel trifluoromethanesulfonate, magnesium bromide, copper bromide, zinc bromide, nickel bromide, magnesium iodide, copper iodide, zinc iodide, nickel iodide, magnesium acetylacetonate, copper acetylacetonate, zinc acetylacetonate, nickel acetylacetonate, and mixtures thereof.

5. The method of claim 4 wherein the metal complex comprises magnesium trifluoromethanesulfonate.

6. The method of claim 1 or 2 wherein the base is selected from the group consisting of triethylamine, diisopropylethylamine, 2,6-lutidine, N-methylmorpholine, N-ethylpiperidine, imidazole, and 5,6-dimethylbenzimidazole.

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7. The method of claim 1 or 2 wherein the ligand has a structure

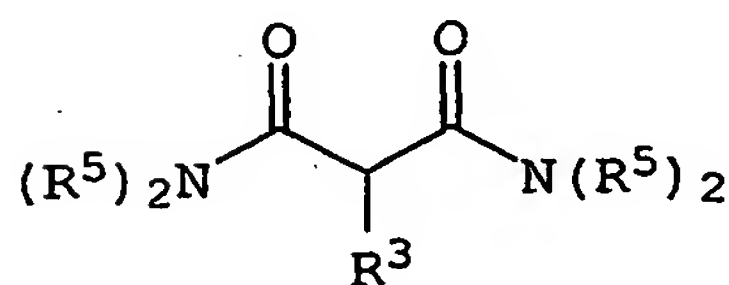
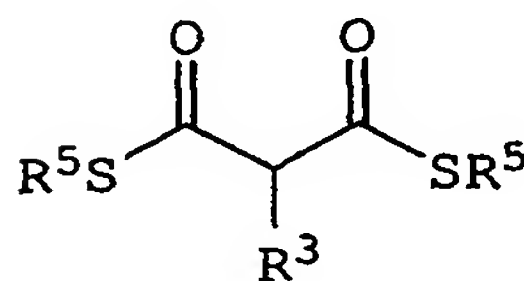
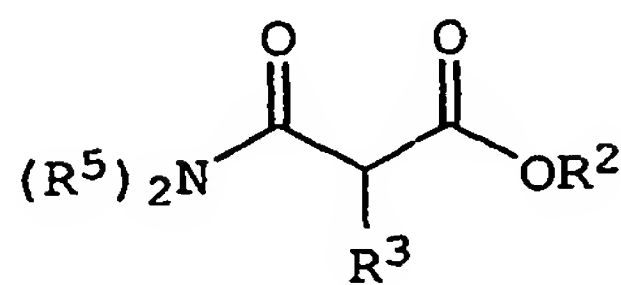
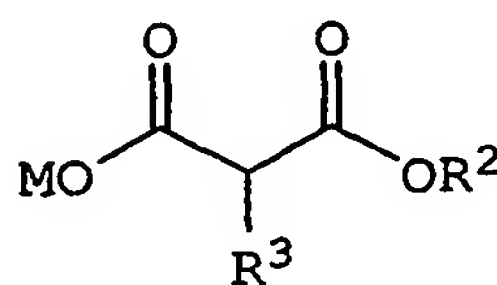
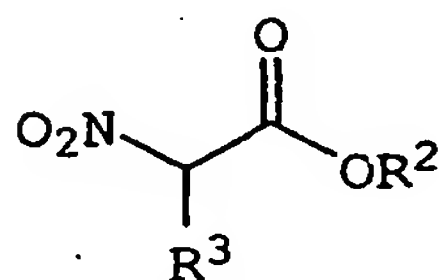
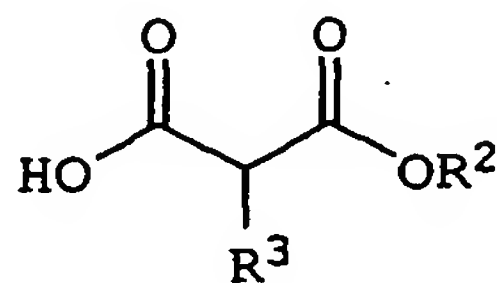


or its enantiomer.

8. The method of claim 2 wherein  $R^6$  and  $R^7$  are alkoxy.

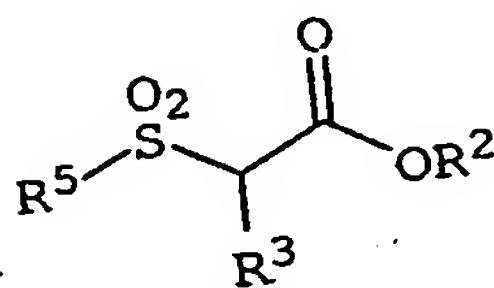
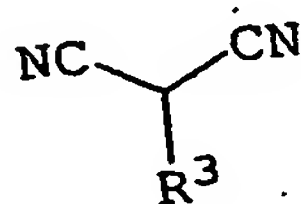
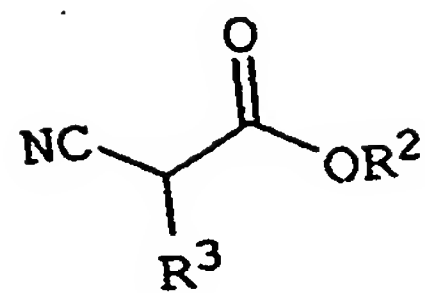
9. The method of claim 8 wherein  $R^6$  and  $R^7$ , independently, are methoxy or ethoxy, and  $R^3$  is methyl or ethyl.

10. The method of claim 1 wherein the compound of structural formula (I) has a structural formula

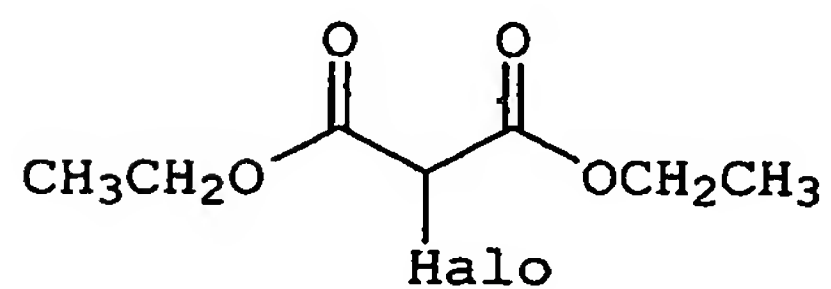
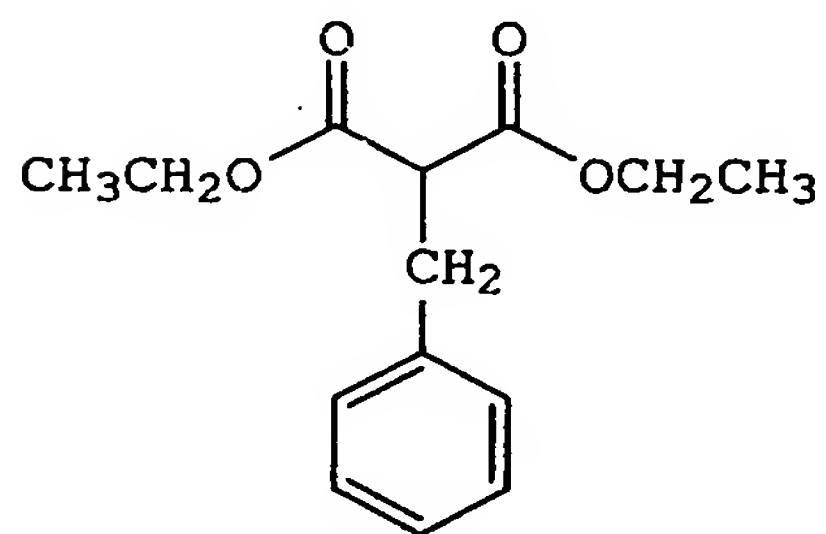
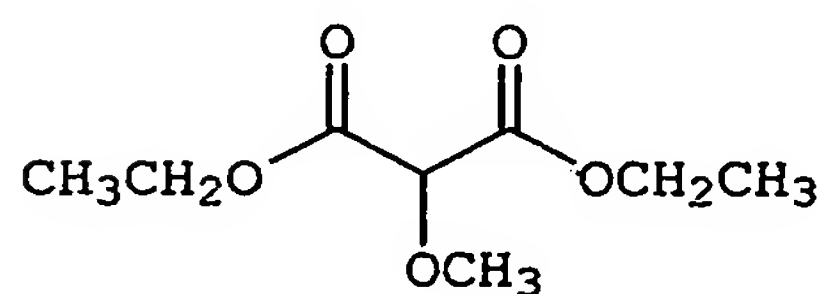
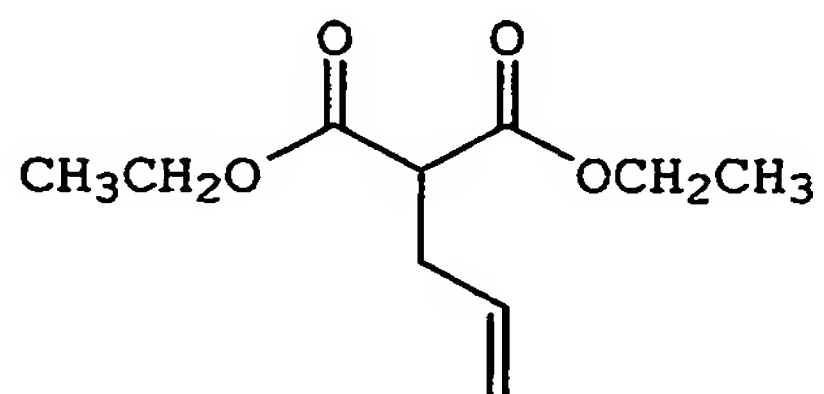
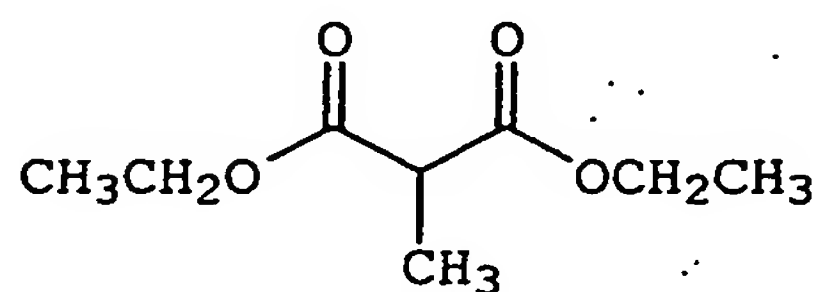
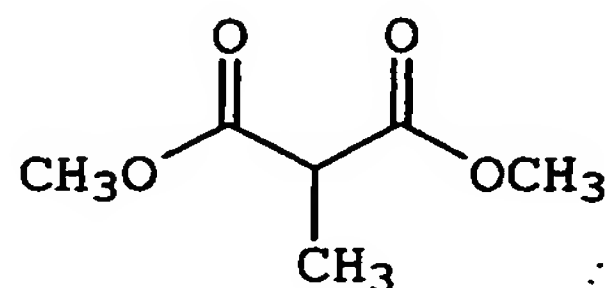




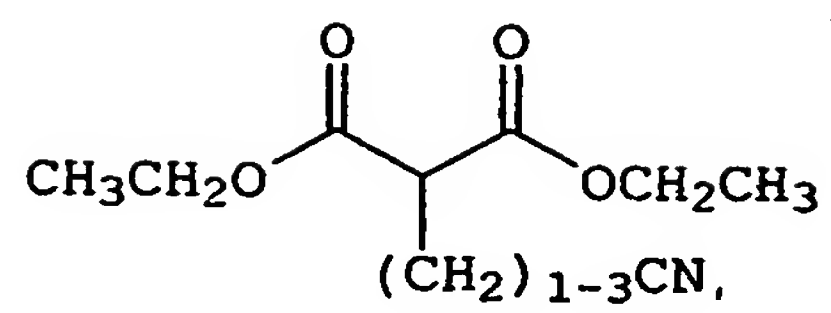
- 58 -



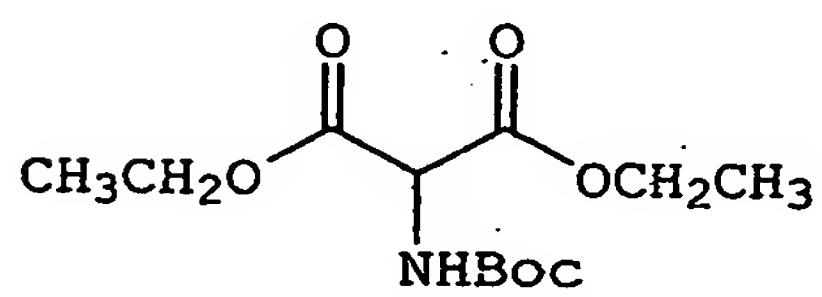
11. The method of claim 2 wherein the  $\alpha$ -substituted  $\beta$ -carbonyl compound has a structural formula:



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, or

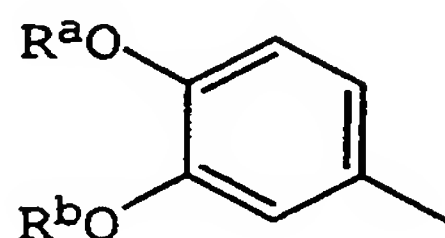


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12. The method of claim 1 or 2 wherein  $R^4$  is aryl.

13. The method of claim 12 wherein  $R^4$  is substituted phenyl.

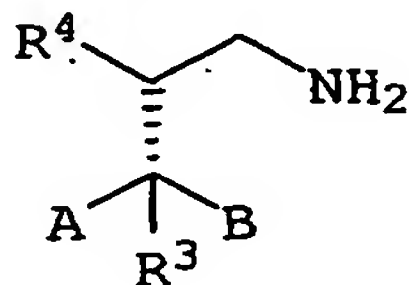
14. The method of claim 1 or 2 wherein  $R^4$  is



wherein  $R^a$  and  $R^b$ , independently, are selected from the group consisting of  $C_{1-4}$ alkyl, cycloalkyl, heterocycloalkyl, aryl, heteroaryl,  $C_{1-3}$ alkylenearyl, and hetero $C_{1-3}$ alkylenearyl.

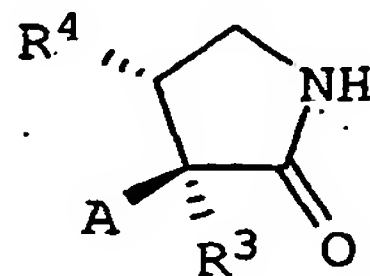
- 62 -

15. The method of claim 1 further comprising the steps of converting the nitro group of nitro compound (III) to form an amino compound (IV)



(IV)

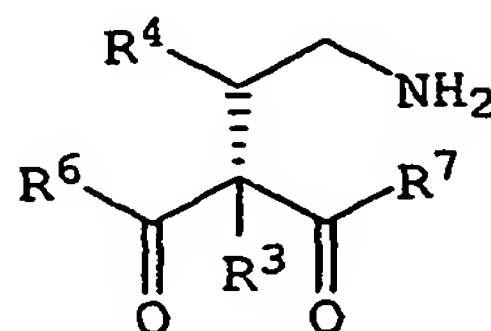
followed by an intramolecular cyclization reaction to form a compound (V)



(V)

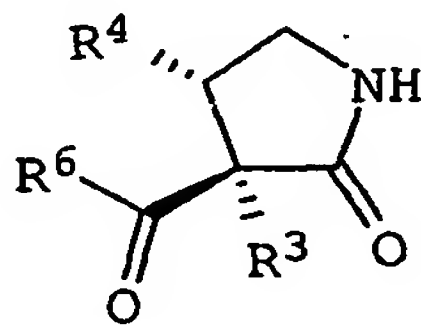
- 63 -

16. The method of claim 2 further comprising the steps of converting the nitro group of nitro compound (IIIa) to form an amino compound (IVa)



(IVa)

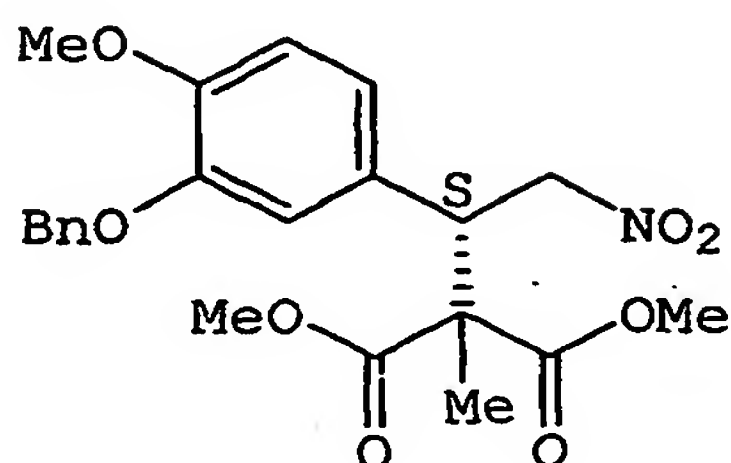
followed by an intramolecular cyclization reaction to form a compound (Va)



(Va)

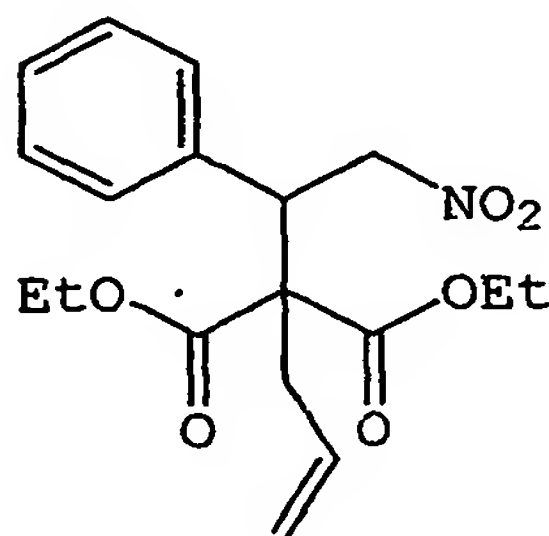
- 64 -

17. The method of claim 16 wherein compound (IIIa) has a structure



wherein Me is methyl and Bn is benzyl.

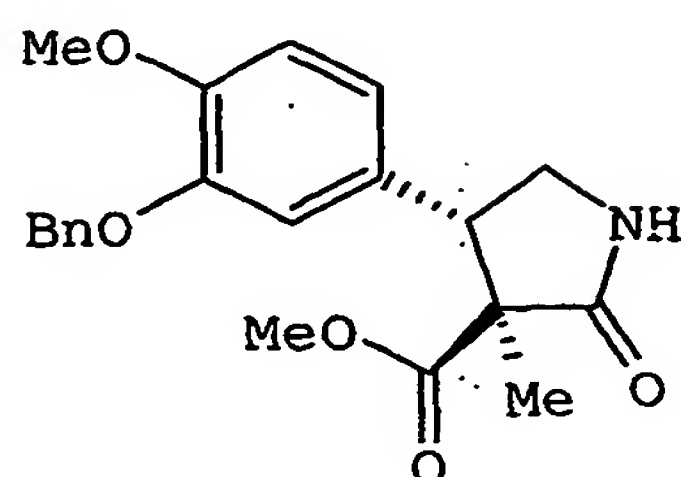
18. The method of claim 16 wherein compound (IIIa) has a structure



wherein Et is ethyl.

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19. The method of claim 16 wherein compound (Va) has a structure



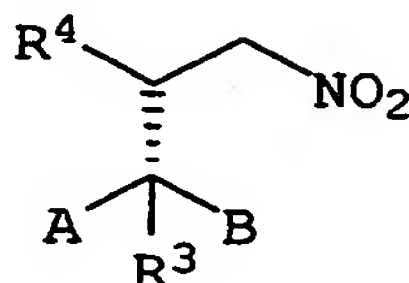
wherein Me is methyl and Bn is benzyl.

20. A compound prepared by the method of any of claims 1 through 19.



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21. A compound having a structural formula (III)

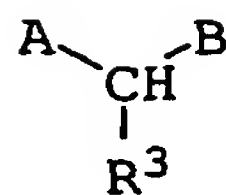


(III)

wherein A is selected from the group consisting of  $\text{C}(=\text{O})\text{OR}^1$ ,  $\text{C}(=\text{O})\text{N}(\text{R}^5)_2$ ,  $\text{C}(=\text{O})\text{SR}^5$ , CN,  $\text{NO}_2$ , and  $\text{SO}_2\text{R}^5$ ; B is selected from the group consisting of  $\text{C}(=\text{O})\text{OR}^2$ ,  $\text{C}(=\text{O})\text{N}(\text{R}^5)_2$ ,  $\text{C}(=\text{O})\text{SR}^5$ , and CN;  $\text{R}^1$  is selected from the group consisting of  $\text{C}_{1-4}$ alkyl, hydro, and M;  $\text{R}^2$  is selected from the group consisting of hydro, M, alkoxyalkyl, alkyl, cycloalkyl, aryl,  $\text{C}_{1-3}$ alkylenearyl, heteroaryl, and  $\text{C}_{1-3}$ alkyleneheteroaryl;  $\text{R}^3$  is selected from the group consisting of  $\text{C}_{1-4}$ alkyl, alkoxy, acylamino, halo, alkylthio, allyl,  $\text{C}_{1-3}$ alkylenearyl, and cyano $\text{C}_{1-3}$ alkyl;  $\text{R}_4$  is selected from the group consisting of unsubstituted or substituted aryl and heteroaryl;  $\text{R}^5$ , independently, is selected from the group consisting of hydro,  $\text{C}_{1-4}$ alkyl, cycloalkyl, aryl,  $\text{C}_{1-3}$ alkylenearyl, heteroaryl, and  $\text{C}_{1-3}$ alkyleneheteroaryl; and M is an alkali metal cation or an alkaline earth metal cation;

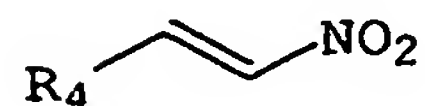
said compound (III) prepared by a method comprising reacting a compound having a structural formula (I)

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(I)

with a nitroolefin of structural formula (II),

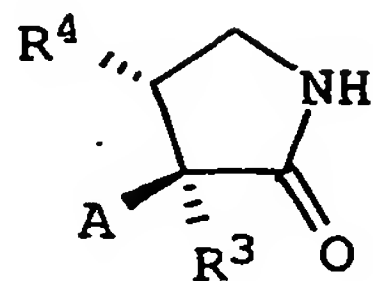


(II)

said reaction performed in the presence of a base and a catalyst complex comprising a ligand and a metal complex.

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22. A compound having a structural formula (V)

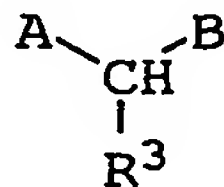


(V)

wherein A is selected from the group consisting of  $C(=O)OR^1$ ,  $C(=O)N(R^5)_2$ ,  $C(=O)SR^5$ , CN,  $NO_2$ , and  $SO_2R^5$ ;  $R^1$  is selected from the group consisting of  $C_{1-4}$ alkyl, hydro, and M;  $R^3$  is selected from the group consisting of  $C_{1-4}$ alkyl, alkoxy, acylamino, halo, alkylthio, allyl,  $C_{1-3}$ alkylenearyl, and cyano- $C_{1-3}$ alkyl;  $R_4$  is selected from the group consisting of unsubstituted or substituted aryl and heteroaryl;  $R^5$ , independently, is selected from the group consisting of hydro,  $C_{1-4}$ alkyl, cycloalkyl, aryl,  $C_{1-3}$ alkylenearyl, heteroaryl, and  $C_{1-3}$ alkyleneheteroaryl; and M is an alkali metal cation or an alkaline earth metal cation;

said compound (V) prepared by a method comprising the steps of:

(a) reacting a compound of structural formula (I)



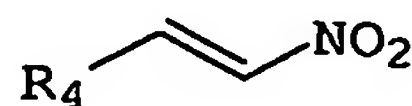
(I)

wherein B is selected from the group consisting of  $C(=O)OR^2$ ,  $C(=O)N(R^5)_2$ ,  $C(=O)SR^5$ , CN, and

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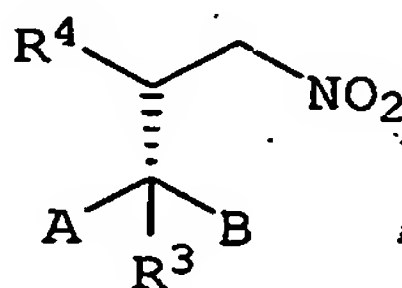
NO<sub>2</sub>; and R<sup>2</sup> is selected from the group consisting of hydro, M, alkoxyalkyl, alkyl, cycloalkyl, aryl, C<sub>1-3</sub>alkylenearyl, heteroaryl, and C<sub>1-3</sub>alkyleneheteroaryl;

with a nitroolefin of structural formula (II)



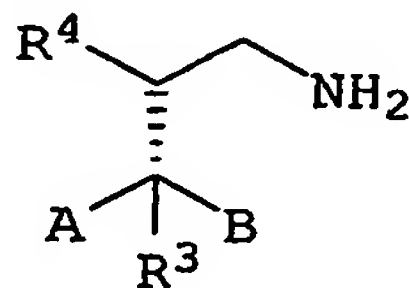
(II)

said reaction performed in the presence of a base and a catalyst complex comprising a ligand and a metal complex to form a compound having a structural formula (III)



(III)

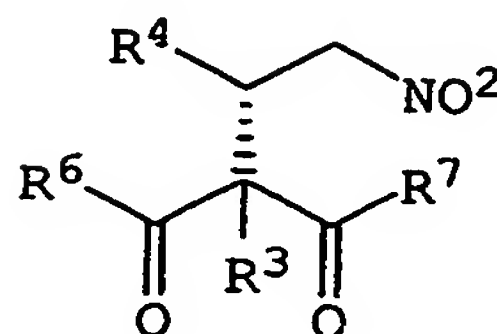
(b) converting the nitro group of compound (III) to form an amino compound (IV)



(IV)

followed by (c) an intramolecular cyclization reaction to form the compound (V).

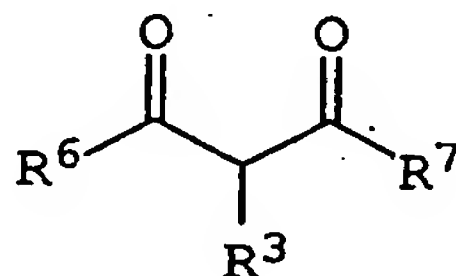
23. A compound having a structural formula (IIIa)



(IIIa)

wherein R<sup>6</sup> is alkoxy, amino, or thio; R<sup>7</sup> is selected from the group consisting of alkoxy, alkoxyalkyl, alkyl, cycloalkyl, aryl, C<sub>1-3</sub>alkylene-aryl, heteroaryl, and C<sub>1-3</sub>alkyleneheteroaryl; R<sup>3</sup> is selected from the group consisting of C<sub>1-4</sub>alkyl, alkoxy, acylamino, halo, alkylthio, allyl, C<sub>1-3</sub>alkylenearyl, and cyanoC<sub>1-3</sub>alkyl; and R<sup>4</sup> is selected from the group consisting of unsubstituted or substituted aryl and heteroaryl;

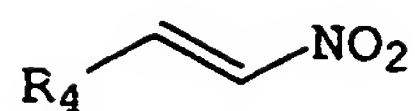
said compound (IIIa) prepared by a method comprising the step of reacting an  $\alpha$ -substituted  $\beta$ -dicarbonyl compound of structural formula (Ia)



(Ia)

with a nitroolefin of structural formula (II),

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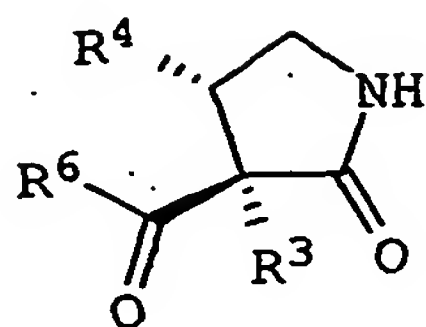


(II)

said reaction performed in the presence of a base and a catalyst complex comprising a ligand and a metal complex.

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24. A compound having a structural formula (Va)

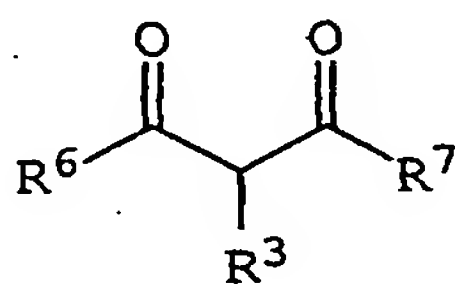


(Va)

wherein  $R^6$  is alkoxy, amino, or thio;  $R^3$  is selected from the group consisting of  $C_{1-4}$ alkyl, alkoxy, acylamino, halo, alkylthio, allyl,  $C_{1-3}$ alkylenearyl, and cyano $C_{1-3}$ alkyl; and  $R^4$  is selected from the group consisting of unsubstituted or substituted aryl and heteroaryl;

said compound (Va) prepared by a method comprising the steps of:

(a) reacting an  $\alpha$ -substituted  $\beta$ -dicarbonyl compound of structural formula (Ia)

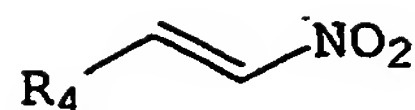


(Ia)

wherein  $R^7$  is selected from the group consisting of alkoxy, alkoxyalkyl, alkyl, cycloalkyl, aryl,  $C_{1-3}$ alkylenearyl, heteroaryl, and  $C_{1-3}$ alkyleneheteroaryl;

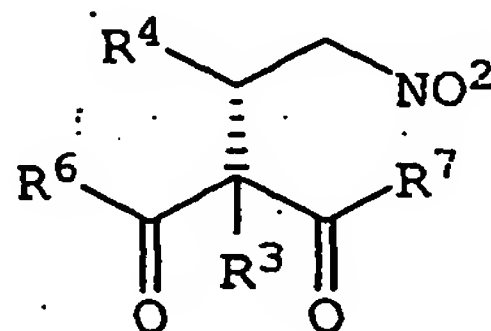
with a nitroolefin of structural formula (II)

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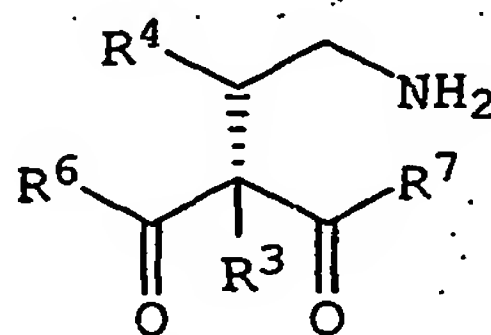
(II)

said reaction performed in the presence of a base and a catalyst complex comprising a ligand and a metal complex to form a compound having a structural formula (IIIa)



(IIIa)

(b) converting the nitro group of compound (IIIa) to form an amino compound (IVa)



(IVa)

followed by (c) an intramolecular cyclization reaction to form the compound (Va).